



Role of water in the CO oxidation reaction on Au/CeO₂: Modification of the surface properties

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ABSTRACT

A metallic monolith coated with 1% Au/CeO₂ catalyst has been calcined at 300 °C and tested in the CO oxidation reaction both in “dry” and “wet” conditions. The light-off curves show a positive effect of the presence of water in the reactive feed on the catalytic activity. With the aim to explain these observations, a FTIR CO adsorption study at liquid nitrogen temperature was performed over a similar powder catalyst. At this low temperature the oxygen mobility from the bulk to the surface is minimized and then surface phenomena are evidenced. Both, the effect of different pre-treatments of the catalysts and the presence of pre-adsorbed water on the surface have been examined. The studies reveal that the previous treatment of the sample deeply affects the surface species and the gold particle size. The water addition provokes oxidation of the surface and improves the CO oxidation activity.

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1. Introduction

The lack of sustainability of the current energy system makes it necessary to develop and adopt alternative energy models. One of these is what is known as the hydrogen economy, based on the use of hydrogen as a carrier of the energy generated from renewable sources. In this process several reactions are involved [1]. The first step, the reforming reactions (hydrocarbons, alcohols, sugars, etc.), [2–6] is followed by processes resulting in hydrogen purification that allows the use of the produced hydrogen (with CO concentration below 10 ppm) as a vector for energy generation in fuel cells [7–9]. Therefore, the reactions for elimination of CO such as TOX (total oxidation) [10,11], PrOX (preferential oxidation) [12–14] and WGS (water gas shift) [15–17] are of paramount importance for the development of clean energy sources based on the hydrogen economy.

The use of monolithic catalysts in all these processes is attractive because they present some advantages compared with powder catalysts, such as better catalytic performance, safer operating conditions and easier catalysts separation. From all of

this, the interest of monolithic devices has increased exponentially in the last years, and a large quantity of works devoted to study different aspect of them, such as the nature of the substrate and catalysts, the coating procedure, etc. appeared [18,19].

Gold-based catalysts are known by their high activity towards CO oxidation at low temperature [10,20]. The nature of the support and the gold particle size are among the most important factors affecting the activity of these systems [15,20,21]. Transition metal oxides such as α -Fe₂O₃, TiO₂ and lately CeO₂ [22] are considered as active supports due to their good redox properties. In spite of the great number of works focused to CO oxidation using Au/CeO₂ catalysts, there is not agreement about the nature of the active sites, the explanation of the observed changes in the activity after successive reaction cycles, and the role of water on the reaction. The presence of chlorine, gold sintering or even gold redispersion has been related with these phenomena [23–26]. In this way, the characterization of the surface after different treatment results an important aspect related to the mechanism of reaction. Concerning the water effect, Boccuzzi et al. [27] concluded that the small amounts of water promote the catalytic reaction of a gold titania catalyst in such a way that the reaction rate passes through a maximum at water concentration of 200 ppm. This benefic effect of the water has also been detected by Bongiorno and Landman [28] from theoretical calculations. These authors proposed the water-

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oxygen co-adsorption provokes a decreasing of activation barrier of CO oxidation on gold nanoclusters. Date and Haruta [29] have also detected that the optimal water concentration in a flow of CO and oxygen is 200 ppm, suggesting that higher concentrations of H₂O provoke the blocking of the active sites. Nevertheless, it is interesting to determine the sites of adsorption of water and the modifications induced on the surface by this molecule influencing the CO adsorption and as consequence the activity of the oxidation.

CO adsorption at low temperature followed by FTIR has traditionally been used to characterise metallic oxides [30,31] and zeolites [32,33]. CO is also able to interact with Lewis acid sites. Stretching mode of gaseous CO molecule (2143 cm⁻¹) shifts to higher or lower wavenumbers depending on the acceptor or donor character of the surface sites interacting with it. Thus, a detailed analysis of CO adsorption spectra can provide fine information on the oxidation and coordination states of the surface sites, their surroundings, etc. At low temperatures, adsorption is favoured and almost all surface sites can be monitored by CO. Few exceptions exists: thus, it is well established that some metallic gold sites are highly inert and do not form carbonyl species thus remaining invisible by FTIR spectroscopy of adsorbed CO [30]. Low temperature favours the interaction of CO with the hydroxyls groups, and the spectroscopic consequences are the shift of $\nu(\text{OH})$ towards lower frequencies and a modification of the $\nu(\text{CO})$ to higher frequencies than gas phase CO. The shift of the O–H stretching gives a measure of acidic strength of hydroxyls groups [32]. These bands are characterized by a very low stability disappearing under vacuum even at low temperature.

In this work we have studied the activity in CO oxidation of stainless steel monoliths coated with 1% Au/CeO₂ catalyst both in “dry” and “wet” conditions. Since the hydrodynamic conditions in both catalytic tests are similar, the observed differences in activity should be due to differences in the surface species. As said above, FTIR CO adsorption at low temperature is an ideal technique to characterize the sites on the surface. However, due to the opacity of the stainless steel substrate, it is not possible to study the monolithic sample by this technique. Thus, the study has been carried out over a powder catalyst with the same composition and prepared by a similar way than the catalytic layer deposited on the metallic monolith. CO adsorption experiments have been carried out on the oxidized and reduced samples both in “wet” and “dry” conditions. The main objective of this work is to contribute to clarify the role of the water, characterising the surface of the catalysts in “wet” and “dry” conditions, both in the oxidised and reduced sample. The characterisation has been carried out using CO adsorption at low temperature, followed by FTIR spectroscopy, which is a widely used technique in this field. The results evidence the sites of adsorption of the water and the induced changes on the surface (generation of active species on CO oxidation) in the studied conditions.

2. Experimental

2.1. Catalyst preparation

2.1.1. Monoliths

Stainless steel monolith was built from AISI 304 austenitic grade by rolling around a spindle alternate flat and corrugated sheets. The final form is a cylinder of 30 mm height and 16 mm diameter. The monolith as obtained was treated in a 10 mL min⁻¹ flow of synthetic air and heated from room temperature (RT) to 900 °C (at 10 °C min⁻¹) and maintained at this temperature during 1 hour. This treatment permits to obtain an adequate surface to the ulterior coating. The coated monolith was obtained after immersion in a colloidal solution of cerium acetate (Nyacol, 10 wt.%) and

gold(III)acetate (Alfa Aesar 99.99%) with a composition calculated to obtain a gold concentration of about 1% weight. The monolith was immersed during 1 min and taken out at constant speed of 3 cm h⁻¹. The excess of colloidal solution was removed by centrifugation at 400 rpm for 10 min. Then, the monolith was dried and calcined at 300 °C (Au–300–M) for 4 h at a heating rate of 2 °C min⁻¹. A more detailed description of the monolithic sample preparation is given in a previous paper [19].

2.1.2. Powder catalyst

The powder sample was prepared using a non-conventional synthesis procedure for supported gold catalysts. As previously described for monolith preparation, a commercial colloidal solution of cerium acetate was used as ceria precursor and the adequate amount of gold(III)acetate to obtain a gold concentration of about 1% weight in the final solid was added to it. After mixing, the resulting suspension was oven dried at 80 °C. The obtained solid was calcined at 300 °C (Au–300) for 4 h. This preparation method allows obtaining Au/CeO₂ catalysts similar to those deposited on stainless steel metallic monoliths [19,34]. The use of chloroauric acid as source of gold is avoided, since chloride ions attack the stainless steel surface producing pitting corrosion.

2.2. Catalyst characterization (powder)

X-ray diffraction (XRD) patterns were recorded using a X'Pert Pro Philips diffractometer working with Cu K α radiation ($\lambda = 1.5404 \text{ \AA}$) in continuous scan mode from 20° to 80° of 2θ using 0.05° sampling interval and 1.0 s.

Chemical composition of catalyst was determined by X-ray fluorescence (XRF) with a Siemens SRS 3000 sequential spectrophotometer equipped with a rhodium tube. XRF measurements were performed onto pressed pellets (sample included 10 wt.% of wax).

The BET surface area was measured by nitrogen adsorption at liquid nitrogen temperature in a Micromeritics ASAP 2000 apparatus. Before analysis, the sample was degassed 2 h at 150 °C in vacuum.

2.3. Catalytic tests (monolith)

The activity measurements were carried out in a flow U-shape glass reactor at atmospheric pressure. The monolith was placed into the glass reactor and a reactive flow (3.4% CO and 21% O₂ balanced by helium) was passed thorough it. The total flow was 42 mL min⁻¹ and the quantitative analysis was carried out with a Balzers Omnistar Bentchop mass spectrometer. The monolith was activated in a flow containing 21% O₂ in helium (total flow 30 mL min⁻¹) at 300 °C during 1 h. Then, the system was cooled down and stabilized at room temperature and the light-off curve (from RT to 300 °C at 5 °C min⁻¹) was started.

With the aim to determine the effect of water in the catalytic activity, a second test was carried out by bubbling the feed through a water saturator at 25 °C.

It is needed to point that even if the gas flow used in the reaction with monolith catalysts are not very appropriated, the positive effect of the water is evidenced. The diffusional limitations in these conditions affect similarly in wet and dry conditions. Moreover, the same effect was observed when the reaction was carried out using the powder catalysts (results not shown in this work).

2.4. FTIR-CO adsorption at low temperature

FTIR spectra of powder catalyst were recorded on a Nicolet Avatar 360 Spectrometer accumulating 64 scans at a spectral

resolution of 2 cm^{-1} . Prior to the experiments, the sample powder was pressed into a self-supporting wafer (density $10\text{--}12\text{ mg cm}^{-2}$) under a pressure of $10^6\text{--}10^7\text{ Pa}$. Due to the high level of noise obtained for the pure samples, they were mixed with silica in a 1:1 ratio. The silica is an inert support and it is reasonably assumed that does not modify the activity of the catalyst. Even with this procedure the noise level remained higher than usually observed with other samples.

The CO adsorption was carried out at low temperature on the fresh sample and on pre-treated ones (oxidized and reduced). The pre-treatments were carried out in air (oxidation) or hydrogen (reduction), heating to $300\text{ }^\circ\text{C}$ and maintained at this temperature during 1 h. Then, the sample was evacuated and cooled to the liquid nitrogen temperature and CO was admitted into the cell recording spectra with time until surface saturation. In order to obtain information about stability of the adsorbed species, sample was degassed under vacuum. After that, a pressure of water of about 400 Pa was introduced into the cell. Ulterior evacuation at RT allows obtaining a “wet” surface on which CO adsorption was again performed. The spectra were recorded at the same conditions after each pretreatment, which permits comparing the surface state in all the cases.

Both the pre-treatment and the experiments were performed *in situ* using a purpose-made IR cell connected to a vacuum-adsorption apparatus with a residual pressure lower than 10^{-3} Pa . The cell allowed registering the spectra at the temperature interval between -175 K and RT. Carbon monoxide ($>99.997\text{ }\%$ purity) was supplied by Linde AG. Before adsorption, carbon monoxide was passed through a liquid nitrogen trap.

3. Results and discussion

The gold content of the powder sample is 0.84% , and its specific surface area (BET) is $120\text{ m}^2\text{ g}^{-1}$.

The XRD pattern of the catalysts calcined at $300\text{ }^\circ\text{C}$ is presented in Fig. 1. Diffraction peaks corresponding to the cubic La3d antiferroite structure of cerium oxide are observed at $2\theta = 28.5, 33.0, 47.4, 56.2, 59.1, 69.3, 76.5$ and 79.0° . Besides this, diffraction peaks at $2\theta = 38.1, 44.3, 64.5$ and 77.4° appear, being assigned to the $(1\ 1\ 1)$, $(2\ 0\ 0)$, $(2\ 2\ 0)$ and $(3\ 1\ 1)$ planes of metallic gold, respectively. The size of ceria and gold crystallites on the sample calcined at $300\text{ }^\circ\text{C}$ are calculated to be 6 and 21 nm , respectively, applying the Scherrer equation. The results show that, as usually observed with supported gold catalysts [35], calcinations of the sample even in presence of oxygen has

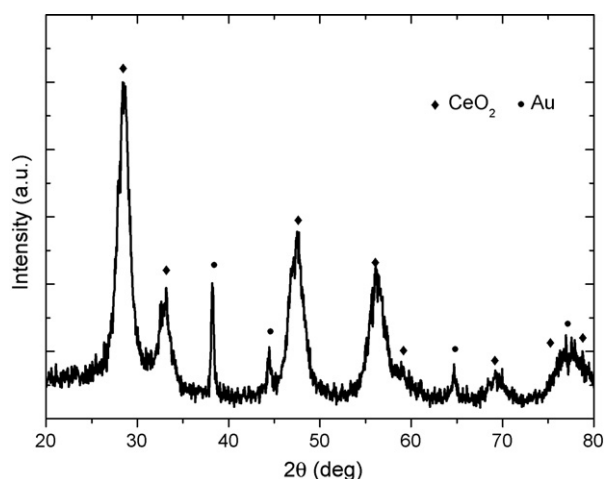


Fig. 1. XRD pattern of the Au/CeO₂ catalyst after calcination at $300\text{ }^\circ\text{C}$.

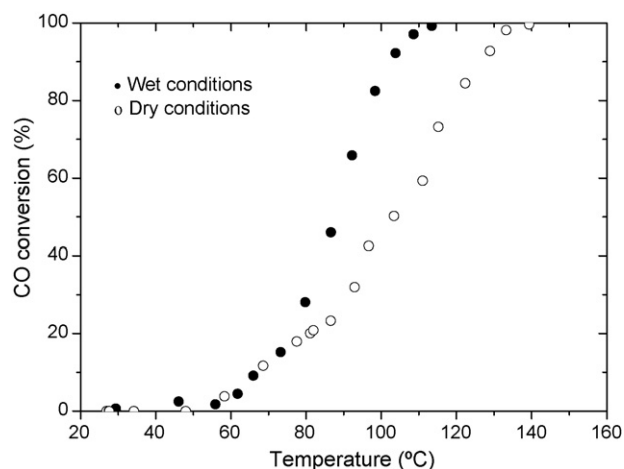


Fig. 2. CO light-off curves of the monolithic catalyst.

led to autoreduction of gold and formation of metal gold particles.

3.1. Catalytic tests

The light-off curves of the studied monolith are shown in Fig. 2. The monolith without catalysts shows no activity. The catalytic activity of our system is not very high compared with that previously reported for gold-ceria catalysts. This fact may be due to the high metal particle size (21 nm) probably related with the non-conventional preparation method used, which is mainly focused to prepare catalytic layers on metallic substrates.

An improvement of activity in “wet” conditions is only detected at temperatures higher than $80\text{ }^\circ\text{C}$, while at lower temperatures both light-off curves are similar. This fact suggests that the presence of water provokes a modification of the catalyst properties as the temperature increases. In order to verify this, the next part of this work has been devoted to the surface characterization by CO adsorption followed by FTIR spectroscopy. On the other hand, no hydrogen production is observed in both wet and dry conditions, pointing out the absence of the water gas shift in our system.

3.2. FTIR experiments

Considering that the studied samples were mixed with silica, it is needed to note that CO adsorption at low temperature on SiO_2 generates two bands in the IR spectra around 2158 and 2140 cm^{-1} . The first one is due to the CO interaction with hydroxyls groups of the silica forming H-bonded species [36] and the second one has been attributed to weakly adsorbed CO (physisorbed molecules [36,37] which are most probably polarized by oxygen anions [38]). Moreover, it has to be considered that OH groups of ceria do not interact with CO even at low temperature [30]. Therefore, it may be concluded that the observed bands in the carbonyl region will be due to interactions of the probe molecule with gold and cerium ions (in different oxidation states), and to CO weakly adsorbed on silica.

No adsorbed species were observed after adsorption of CO at low temperature on the fresh catalyst suggesting a very low number of active sites to CO adsorption were available at these conditions. It should be noted that carbonyl species were observed on sample pre-treated at $300\text{ }^\circ\text{C}$ under air or hydrogen (see below). The presence of adsorbed water on the surface of non activated samples leads to blocking of some CO adsorption sites. However,

ionic or metal sites able to form back π -bond with CO are usually monitored even on water-precovered samples [39]. Such sites on our sample could be Au^+ , Au^0 and Au^- species. Therefore, the results indicate that these species either do not exist on the surface or are not accessible to CO. Therefore, we can conclude that the major part of the gold remained as Au^{3+} on the fresh sample. Another explanation of the observed phenomenon is that part of the organic compounds used in the catalyst preparation (acetates) remained after calcination, thus blocking the surface adsorption sites. Another consequence of this effect is the suppression of the sample catalytic activity. The increasing of the temperature and the composition of reactive flow influence the elimination of these organic compounds and should be one of the factors responsible of the activity change observed in the light-off curves. Therefore, the observed higher activity in “wet” conditions for temperatures higher than 80 °C (Fig. 2) suggests the presence of water in the reactive flow favours the surface cleaning.

On the other hand, the vacuum treatment modifies the surface in a similar way eliminating impurities. Therefore, the pre-treatment in the vacuum cell at 300 °C allows eliminating the majority of these organic compounds, making possibly to detect the active sites on the surface.

As said before, the CO adsorption has been carried out on oxidised and reduced sample (both in “dry” and “wet” conditions).

3.2.1. CO adsorption on “dry” samples

Adsorption of CO (650 Pa equilibrium pressure) at -175 °C on the oxidized sample needs 15 min to achieve the saturation of the surface, indicating the slow kinetic of the interaction CO–surface at this temperature. After saturation (Fig. 3spectrum a), absorption bands at 2170, 2154, 2109 (broad) and a shoulder at 2133 cm^{-1} are observed. A weak band at 2363 cm^{-1} was also detected and assigned to adsorbed CO_2 . Heating the sample to room temperature during evacuation led to a slight increase of this band in intensity. The results suggest that CO oxidation to CO_2 proceeds, most probably with the participation of the oxygen species from the support, and reducing the sample surface.

According to literature data, the band at 2170 cm^{-1} is generated by the interaction of CO with Ce^{4+} sites [40]. In our case, the band at 2170 cm^{-1} easily disappears during evacuation even at -175 °C (Fig. 3, spectra a–i) and a new band at 2175 cm^{-1} becomes visible. The higher stability of this last band suggests that it is due to Au^+ –CO species, which agrees with the attribution of Venkov et al. [41] who proposed this band correspond to carbonyls on isolated Au^+ sites. The band at 2154 cm^{-1} (early disappearing under vacuum) corresponds to the CO interacting with the hydroxyls groups of the silica [36]. The shoulder at 2133 cm^{-1} is due to CO physically

adsorbed [36,37] which is confirmed by the very low stability of these species.

As it is well known, a band at 2127 cm^{-1} is ascribed to the forbidden $^2F_{5/2} \rightarrow ^2F_{7/2}$ electronic transition of Ce^{3+} ions [42,43]. In a previous work [44], we have detected bands at 2109 and 2125 cm^{-1} showing a different evolution during the catalyst reduction by CO in an Au/CeO₂ catalyst. We concluded that the existence of cerium surface sites adjacent to gold atoms is responsible of the band at 2110 cm^{-1} , while the isolated Ce^{3+} species generate the band at 2127 cm^{-1} . Bands around 2110 cm^{-1} have also been attributed by some authors to CO adsorbed on Au^0 step sites [45]. Since in our experiments, this band remains after evacuation of CO (Fig. 3spectrum i), the relationship between this band and the Ce^{3+} species seems to be the most plausible attribution. However, the observed broad band with maximum at 2109 cm^{-1} and a tail of absorption around 2120 cm^{-1} in the present work may include bands representing both species (spectra deconvolution is difficult in this case). Taking into account both the vacuum treatment and the reducing character of CO, one can accept that a certain quantity of cerium appears in its reduced form (Ce^{3+}) at the conditions in which the spectra shown in Fig. 3 were collected. Indeed, the band at 2109 cm^{-1} was the only one band in the region resisting evacuation (Fig. 3spectrum i) which confirms the attribution of this band to reduced cerium sites. Moreover, since the most stable carbonyl species is that related with the band at 2175 cm^{-1} (CO adsorbed on Au^+ species) and as CO_2 is detected, we tentatively propose that the oxidized gold species are active in these conditions. This idea has been previously suggested [43].

When CO was adsorbed on the reduced sample in absence of water, bands at 2158 cm^{-1} (with shoulders at 2149 and 2136 cm^{-1}) and at 2088 cm^{-1} were observed (Fig. 4spectrum a). No features assignable to adsorbed CO_2 were registered in this case which is consistent with the sample reduction pretreatment. Evacuation leads to a fast disappearance of the bands at 2136 cm^{-1} and then that at 2158 cm^{-1} revealing existence of more stable and less intense bands at 2167 and 2163 cm^{-1} (Fig. 4spectra b–f). The band at 2088 cm^{-1} , although highly resistant towards evacuation, also disappears at RT. The band at 2149 cm^{-1} also corresponds to relatively stable species.

After hydrogen treatment at 300 C, one can expect to find bands corresponding to more reduced species which would appear at lower frequencies. Manzoli et al. [40] have attributed a band at 2163 cm^{-1} to Ce^{x+} –CO species, while other authors found the Au^+ –CO species roughly in the same spectral region (2167 cm^{-1} according to Venkov et al. [41]). In our case is clear from Fig. 4 that the band at 2163 cm^{-1} is more stable than the shoulder at

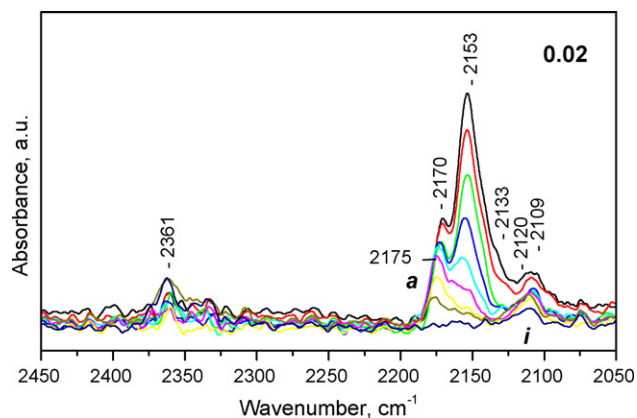


Fig. 3. Difference spectra in evacuation after CO saturation of the oxidized Au/CeO₂ sample in “dry” conditions.

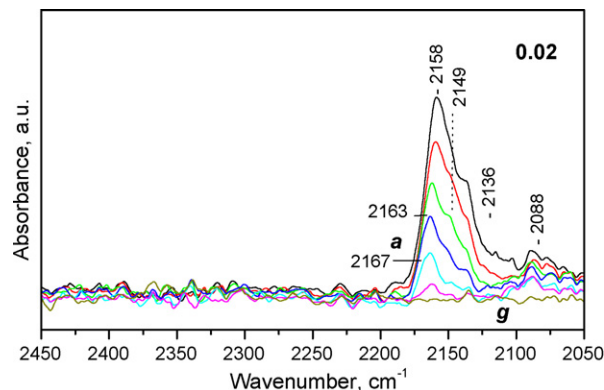


Fig. 4. Difference spectra in evacuation after CO saturation of the reduced Au/CeO₂ sample in “dry” conditions.

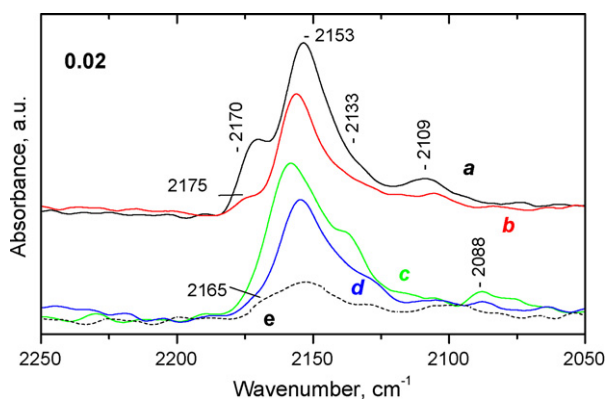


Fig. 5. Difference spectra comparison after surface saturation: (a) oxidised Au/CeO₂ sample in “dry” conditions, (b) oxidised Au/CeO₂ sample in “wet” conditions, (c) reduced Au/CeO₂ sample in “dry” conditions, (d) reduced Au/CeO₂ sample in “wet” conditions and (e) reduced Au/CeO₂ sample in “wet” conditions after 10 s of evacuation.

2167 cm⁻¹. Therefore, we attribute the band at 2163 cm⁻¹ to CO adsorbed on oxidised gold species and the shoulder at 2167 cm⁻¹ to Ce^{x+}-CO species.

Bands at 2158 and 2136 cm⁻¹ are also detected in this experiment, and as before, they are assigned to H-bonded and physically adsorbed CO species respectively. The observed shift of the band corresponding to H-bonded CO species to higher frequencies is most probably provoked by the dehydroxylation of the surface during the reduction which generates more acidic sites [43]. However, we cannot rule out the possibility of modification of silanol groups by cerium species.

The band at 2149 cm⁻¹ was detected only with the reduced sample. According to literature data, the cluster size and the coordination number of gold affect the $\nu(\text{CO})$ frequency [46]. Bands appearing in 2140–2130 cm⁻¹ region have been ascribed [39,47] to Au_n(CO)_m species with 4 ≤ n ≤ 6. In a previous work [44], we have pointed out the reduction at 300 °C by CO of a gold–ceria sample induces the creation of vacancies changing the interaction strength between the gold particles and the support, increasing the gold dispersion. As a consequence, the oxygen mobility from bulk to surface is favoured and a new oxidized species is created. The frequency and the stability of the carbonyls of these species are intermediate between those typical of isolated Au⁺ cations and metallic gold sites. The presence of positively charged gold sites with various coordination environments have been proposed in the literature [33,36,48,49]. In this work, since the sample has previously been reduced by hydrogen at 300 °C, we can reasonably assume a similar effect. From the above it is clear that the pre-treatment appreciably modifies the gold speciation and the activity of the catalyst. The reversibility of this phenomenon in presence of oxygen (CO oxidation conditions) is not clear and complementary experiences are needed to clarify this point.

A band at 2088 cm⁻¹ has also been detected on the reduced sample. It has been reported that carbonyls species on metallic gold appear around 2100 cm⁻¹ being sensible to the gold dispersion [43]. Therefore, we can attribute this band to Au⁰-CO species, evidencing that, at least, a certain proportion of gold has been reduced to metallic gold during the hydrogen treatment. It is however, not excluded the band at 2088 cm⁻¹ to characterize carbonyls of negatively charged Au^{δ-} gold species.

It is important to note that the spectra shown in Figs. 3–5 are difference spectra; the reference spectrum being that of the surface before adsorption. Therefore, the bands in these figures are representative of the modifications occurred in the adsorption–desorption processes. Besides this, the species non-modified during these processes are not seen. Since band at 2109 cm⁻¹ is not appearing in Fig. 4, we conclude that no additional reduction of the surface is produced by the CO adsorption, probably due to the removing of oxygen from the surface during the pre-treatment in hydrogen. No CO₂ has been detected in this case, corroborating that the CO in these conditions does not reduce the surface.

This comparison between the species formed on oxidized and reduced surfaces confirms the bands attribution and reveals the dynamic of the surface in this catalyst. The main idea from these facts is the importance of previous treatment in gold-based catalysts with an “active support”.

3.2.2. CO adsorption on “wet” samples

After CO adsorption, the sample was cleaned by evacuation at room temperature; water was adsorbed and then partially removed by RT evacuation. On this “wet” sample, CO was adsorbed at low temperature to characterize the species on the surface. The comparison between spectra recorded after CO adsorption on “wet” and “dry” surfaces for the oxidized and reduced samples is shown in Fig. 5. Water adsorption produces similar phenomena in both samples: decreasing the intensity of the OH-CO bands at 2154 (oxidized sample) and 2158 cm⁻¹ (reduced sample). It has been pointed out that on hydrated silica samples the CO mainly interacts with free silanols (no H-bonded silanols) [30]. Consequently, the band characterizing the interaction of CO with OH groups of silica shows a lower intensity after water adsorption.

On the other hand, with the “wet” oxidized sample, a decrease in intensity of the bands at 2109 and 2170 cm⁻¹, compared with those registered with the “dry” sample, is observed (Fig. 5, spectra a and b). The lower intensity of the band at 2109 cm⁻¹ indicates an oxidation of Ce³⁺ after water adsorption and the decreasing in the intensity of the band at 2170 cm⁻¹ suggests that water is adsorbed on cerium sites. Au⁺-CO species, responsible of the band at 2175 cm⁻¹ are monitored by CO after water adsorption, consistent with earlier report [42].

In the reduced sample, water adsorption (Fig. 5 spectra c and d) provokes a decrease of the band at 2088 cm⁻¹ (Au⁰-CO or Au^{δ-}-CO species), confirming that in this sample, water also oxidises the

Table 1
Main observations of the IR study carried out on the catalyst

Conditions		IR Observations	
Oxidised	Dry	CO on Ce ⁴⁺ (2170 cm ⁻¹) CO on Au ⁺ (2175 cm ⁻¹) Reduced Ce ³⁺ (2109, 2120 cm ⁻¹)	CO ₂ is produced Surface is reduced
	Wet	CO on Ce ⁴⁺ (2170 cm ⁻¹), lower intensity Reduced Ce ³⁺ (2109, 2120 cm ⁻¹), lower intensity	CO ₂ is produced H ₂ O is adsorbed on cerium sites
Reduced	Dry	CO on Au ⁰ or Au ^{δ-} (2088 cm ⁻¹) Generation Au _n (CO) _m species (2149 cm ⁻¹)	CO ₂ is not detected Gold redispersion
	Wet	CO on Au ⁰ or Au ^{δ-} (2088 cm ⁻¹) CO on Au ⁺ (2175 cm ⁻¹)	CO ₂ is produced Surface reoxidation by H ₂ O

surface. The presence of $\text{Au}^+ \text{--CO}$ species becomes evident during degasification of the sample at low temperature (Fig. 5 spectrum e).

Therefore, we conclude that water may be absorbed on the surface oxidising it. Considering that the oxidised species have been proposed as active species in CO oxidation, the presence of water in the flow of reaction should improve the CO oxidation reaction. For clarity, the main observations and conclusions extracted from them are summarized in Table 1.

4. Conclusions

An improvement of the CO oxidation activity in “wet” conditions is detected at temperatures higher than 80 °C over a 1% Au/CeO₂ catalyst coated on stainless steel monolith suggesting that the presence of water provokes a modification of the catalyst properties as the temperature increases. At temperatures lower than 80 °C, the activity in “wet” and “dry” conditions are similar, which could be related with the presence of leftovers of acetates used in the catalyst preparation; which blocks the active sites.

In situ FTIR CO adsorption studies evidence that the pre-treatment of the catalyst under different atmospheres (oxidant or reductive, presence or absence of water) induces changes in the surface properties (oxidation state of gold and/or cerium species). The reduction pre-treatment results in the dispersion of the gold in the surface of the catalyst. The water is adsorbed on cerium sites oxidizing the catalysts, which generates active species in CO oxidation (Au^+).

These results suggest that the pre-reduction of the catalyst and the presence of water in the flow of reaction are the most interesting conditions to use this type of catalysts in the reaction of CO oxidation.

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